STATE OF CALIFORNIA - CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY
PETE WILSON, *Governor*

AIR RESOURCES BOARD
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MEMORANDUM

TO: Dr. John Sanders, Chief
Environmental Monitoring and Pest Management Branch
Department of Pesticide Regulations

FROM: George Lew, Chief
Engineering and Laboratory Branch

DATE: November 20, 1995

SUBJECT: NALED APPLICATION FINAL REPORT

Attached is the final report, "Ambient Air Monitoring after an Application of Naled in Tulare County During June 1995."

If you or your staff have questions or need further information, please contact me at 263-1630 or Don Fitzell at 263-2041.

Attachment

cc: James Stratton (w/Enclosure)
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Lenord Craft (w/Enclosure)
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State of California
California Environmental Protection Agency
AIR RESOURCES BOARD

AMBIENT AIR MONITORING AFTER AN APPLICATION OF NALED IN TULARE COUNTY DURING JUNE 1995

Engineering and Laboratory Branch
Monitoring and Laboratory Division

Test Report No. C91-031A

Report Date: November 20, 1995

APPROVED:

Don Fitzell, Project Engineer

Cynthia L. Castronovo, Manager,
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George Lew, Chief,
Engineering and Laboratory Branch

Ambient Air Monitoring After an Application of Naled in Tulare County During June 1995

This report presents the results of ambient air monitoring after a ground application of naled at a selected orange grove in Tulare County. Samples were collected before, during and for 72 hours after the start of the application. Samples were analyzed for dichlorvos, the primary breakdown product, as well as naled.

Naled concentrations ranged from 0.0157 ug/m^3 to a maximum concentration of 6.30 ug/m^3, which was measured during the application period. Dichlorvos concentrations ranged from not detected (<0.030 ug/sample, <0.006 ug/m^3 for the 5-hour application period) to a maximum of 0.994 ug/m^3.

Acknowledgments

Ken Lewis was the Instrument Technician. David Todd and Angus MacPhearson of the ARB also assisted in the sampling. Assistance was provided by Lynn Baker, Cara Roderick, and Ruth Tomlin of the ARB's Air Quality Measures Branch as well as the Tulare County Agricultural Commissioner's Office in site selection. Chemical analyses were performed by the staff of the Trace Analytical Laboratory, Department of Environmental Toxicology, University of California, Davis.

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I. INTRODUCTION

The Air Resources Board (ARB) Engineering and Laboratory Branch (ELB) staff conducted three-day source impacted ambient monitoring to determine the concentration of naled (Dibrom) after its application on an orange grove in Tulare County in June 1995. The sampling occurred from June 5 through June 9, 1995. The monitoring was designed to determine levels of naled as well as its primary breakdown product, dichlorvos. This monitoring was requested by the Department of Pesticide Regulation (DPR) as required by the Food and Agricultural Code 14021, in order for DPR to evaluate the persistence and possible human exposure to this pesticide.

The Pesticide Use Report for 1993 indicates naled was most widely used on cotton (27,256 pounds), safflower (24,688 pounds) and oranges (21,161 pounds) in California. Naled is used as an insecticide to control citrus thrips on oranges.

II. DESCRIPTION

Naled (molecular weight 380.79 g/mole) is a white solid with a low melting point, 27°C. At 20° C its vapor pressure is about 2×10^{-3} mm Hg. Naled is practically insoluble in water, but completely hydrolyzed by water within 24 hours. Naled is freely soluble in aromatic and chlorinated hydrocarbons, ketones and alcohols. The LD_{50} in male rats is 250mg/kg orally and 800 mg/kg dermally (The Merck Index, Eleventh Edition).

Dichlorvos is a colorless liquid, boiling point 140°C at 20 mm Hg. The vapor pressure at 20°C is 1.2×10^{-2} mm Hg. It is soluble in dichloromethane, 2-propanol, and toluene, while practically insoluble in water. The oral LD_{50} in male rats is 80 mg/kg. Dichlorvos is subject to the provisions of the Safe Drinking Water and Toxic Enforcement Act (Proposition 65). The 24-hour, ten in one million Proposition 65 risk level is 0.1 ug/m^3 (based on an average breathing rate of 20 m^3 for 24 hours and a 70 year lifetime exposure) (California Code of Regulations, 1994).

III. SAMPLING LOCATIONS

An orange grove of about 20 acres was selected and approved by ARB staff to use for application monitoring. Five samplers, each at about 1.5 meters above ground, were set up (see FIGURE I): two on the southeastern perimeter (site E) at a distance of about 5 yards from the grove, one about 14 yards from the southern perimeter (site S), one about 15 yards from the western side (site W) and one about 5 yards from the northern side (site N). A meteorological station, at a height of about 7 feet, was set up near site N to determine wind speed and direction.

Sites N and E did not meet the siting criteria outlined in the Quality Assurance Plan for Pesticide Monitoring (APPENDIX II, Attachment II). Sampler N was backed up against an abandoned orchard with trees and brush measuring 6 - 10 feet high. The duplicate samplers at Site E were in an orange grove adjacent to the one being monitored. The southeastern portion of the perimeter was chosen because younger, therefore smaller trees were present which minimized their influence on the wind patterns. ARB staff has found it difficult to meet the siting criteria when monitoring orchards because of the close proximity of other orchards. Attempts are made to minimize the effects of adjacent trees to the samplers.

The application was by air-blast sprayer and took about 4 hours. One sprayer was used. It started at the southwestern corner traveling rows which ran west to east. The sprayer completed the rows to finish at the northern end of the orchard. Dibrom 8 was applied at a rate of 1 pint per acre. Carzol SP (an insecticide) was applied with Dibrom 8 at a rate of 1.5 pounds per acre as well as a fertilizer, 10-12-0 at a rate of 0.2 gallons per acre.

IV. SAMPLING METHODOLOGY

The sampling method used during this study required passing measured quantities of ambient air through a Teflon holder containing approximately 30 cc of XAD-4 resin (see APPENDIX I). The resin was held in place by installing stainless steel screens on each side of the resin and between the Teflon support rings. Any naled and dichlorvos present in the sampled ambient air was captured by the XAD-4 adsorbent. Subsequent to sampling, the resin was transferred into a glass jar with a Teflon-lined lid and stored in an ice chest containing dry ice. All samples were transported on dry ice to the Trace Analytical Laboratory (TAL) of the Department of Environmental Toxicology, U.C. Davis for analysis.

Each sample train consisted of an XAD-4 resin holder, Teflon fittings and tubing, control valve, rotometer, train support, and a 12VDC powered vacuum pump. A diagram of the sampling train is shown in

APPENDIX II, Attachment I. Aluminum foil was wrapped around the holder to protect the adsorbent from exposure to sunlight.

The sample pump was started and the flow was adjusted with a metering valve to an indicated reading of 15.0 on the rotometer. A leak check was performed by blocking off the flow meter inlet. Upon completion of a successful leak check, the indicated flow rate was again set at 15.0 and was recorded (if different from the planned setting) along with date, time and site location. Calibration prior to use in the field indicated that an average flow rate of 14.8 lpm was actually achieved when the flow meter was set to 15.0. At the end of each sampling period the final indicated flow rate (if different than the set 15.0), stop date, and time were recorded. If the final flow rate changed from the original 15.0 lpm, the average of the initial and the final flow rates was used to calculate the total volume of sampled air.

V. ANALYTICAL METHODOLOGY

The XAD-4 resin recovered from each sampler was analyzed by the TAL staff. The XAD-4 resin was extracted with 50 ml ethyl acetate followed by gas chromatography/nitrogen-phosphorus detection. Separation was accomplished on a DB-5 Megabore capillary column. A description of the complete analytical methodology can be found in "Method Development for Naled and Dichlorovos in Air Samples Using XAD-4 Resin as a Trapping Medium." (APPENDIX I).

VI. RESULTS

The monitoring results for naled are shown in TABLE I. The monitoring results for dichlorvos are shown in TABLE II. A summary of the on-site meteorological data is presented in TABLE III. A summary of the monitoring and meteorological data for naled and dichlorvos is presented in TABLE IV and TABLE V, respectively. Additional detailed meteorological data from the Porterville Airport is presented in APPENDIX III. None of the results presented in this report have been corrected for percentage recovery.

Naled concentrations ranged from 0.0157 ug/m^3 to a maximum concentration of 6.30 ug/m^3, which was measured during the application period. Dichlorvos concentrations ranged from not detected (<0.030 ug/sample, <0.006 ug/m^3 for the 5-hour application period) to a maximum of 0.994 ug/m^3. These values are significantly higher than those found in an urban ambient monitoring program conducted earlier in Tulare County (Airborne Concentrations of Naled and Dichlorvos in Central Tulare County from Sampling Conducted in May and June 1991). The

maximum naled value for the ambient study was 0.077 ug/m^3 while the maximum dichlorvos value was 0.059 ug/m^3.

VII. QUALITY ASSURANCE

Reproducibility, linearity, collection and extraction efficiency, minimum detection limit and storage stability are described in the Method Development for Naled and Dichlorovos in Air Samples Using XAD-4 Resin as a Trapping Medium (APPENDIX I).

All of the procedures outlined in the Quality Assurance Plan (APPENDIX II, Attachment II) were followed except: the sampling schedule was modified to avoid collection of a sample in the middle of the night, no field spikes were prepared, and all of the sites did not meet the criteria in the QA Plan. In addition, a flow rate audit, a systems audit and an analytical performance audit were performed by the Quality Management and Operations Support Branch (QMOSB) (APPENDIX IV).

The TAL also ran validation (spiked) samples prepared in-house. Recoveries ranged from 95% to 116% for dichlorvos and 83% to 124% for naled.

FIGURE I. Naled Monitoring Sites

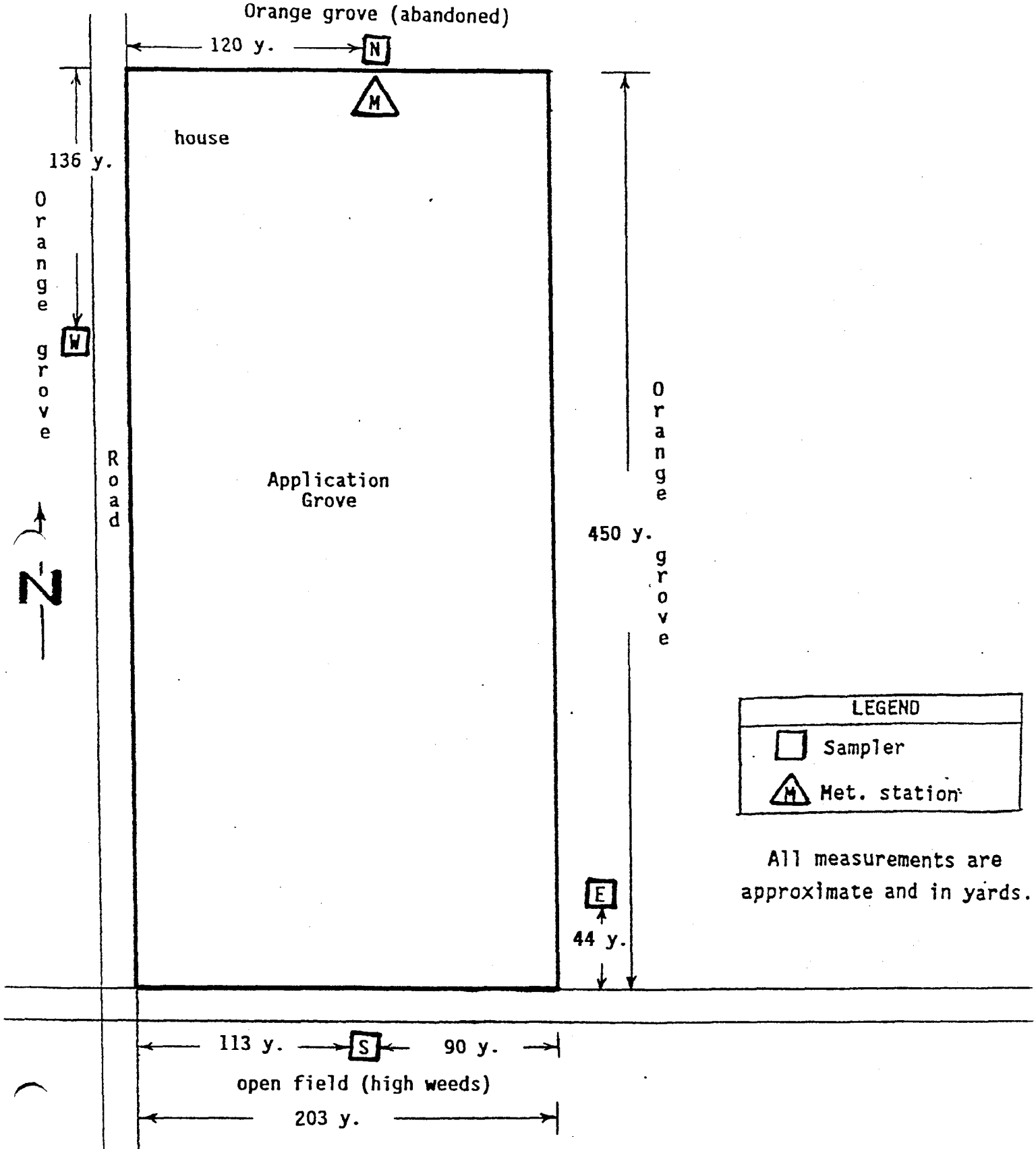


TABLE I. Naled Application Monitoring Data

Sample ID	Time (min.)	Volume[1] (m^3)	Total (ug)	Concentration (ug/m^3)	Collection Time (Approx.)
0S	640	9.47	ND	--	
0E-1	645	9.55	ND	--	Background
0E-2	645	9.55	ND	--	
0N	650	9.62	ND	--	6/5-6/95
0W	645	9.55	ND	--	(1900-0600)
1S	340	5.03	0.231	0.0459	
1E-1	335	4.96	15.48	3.12	Application
1E-2	335	4.96	14.51	2.93	
1N	330	4.88	30.75	6.30	6/6/95
1W	335	4.96	6.12	1.23	(0630-1130)
2S	105	1.55	0.106	0.0684	
2E-1	105	1.55	0.53	0.342	
2E-2	105	1.55	0.69	0.445	
2N	110	1.63	1.38	0.847	
2W	100	1.48	0.134	0.0905	6/6/95
2B	BLANK	--	ND	--	(1130-1330)
3S	180	2.21*	0.32	0.145	
3E-1	180	2.66	0.48	0.180	
3E-2	180	2.66	0.46	0.173	
3N	180	2.66	0.36	0.135	6/6/95
3W	185	2.74	0.043	0.0157	(1330-1630)
4S	195	2.89	0.15	0.0519	
4E-1	195	2.89	0.15	0.0519	
4E-2	195	2.89	0.075	0.0260	
4N	190	2.81	0.10	0.0356	6/6/95
4W	195	2.89	ND	--	(1630-1930)
5S	690	10.2	4.59	0.450	
5E-1	695	10.3	1.15	0.112	
5E-2	695	9.90*	1.14	0.115	
5N	690	9.35*	20.21	2.16	6/6-7/95
5W	690	10.2	8.82	0.865	(1930-0700)
6S	1440	21.3	22.22	1.04	
6E-1	1435	21.2	3.300	0.156	
6E-2	1435	21.2	3.519	0.166	
6N	1440	19.8*	41.11	2.08	6/7-8/95
6W	1440	21.3	20.28	0.952	(0700-0700)
7S	1450	21.5	2.12	0.0986	
7E-1	1445	20.6*	0.36	0.0175	
7E-2	1445	21.4	0.37	0.0173	
7N	1455	21.5	5.280	0.246	6/8-9/95
7W	1455	21.5	3.12	0.145	(0700-0700)

[1]All flows at 14.8 liters per minute unless otherwise noted.
*Flow had decreased at end of run, volume corrected. See SAMPLING METHODOLOGY.
ND = Not Detected, <0.030 ug/sample.
No values corrected for percentage of recovery.

TABLE II. Dichlorvos Monitoring Data

Sample ID	Time (min.)	Volume[1] (m^3)	Total (ug)	Concentration (ug/m^3)	Collection Time (Approx.)
OS	640	9.47	ND	--	
OE-1	645	9.55	ND	--	Background
OE-2	645	9.55	ND	--	
ON	650	9.62	ND	--	6/5-6/95
OW	645	9.55	ND	--	(1900-0600)
1S	340	5.03	ND	--	
1E-1	335	4.96	2.10	0.423	Application
1E-2	335	4.96	1.99	0.401	
1N	330	4.88	2.48	0.508	6/6/95
1W	335	4.96	0.64	0.129	(0630-1130)
2S	105	1.55	ND	--	
2E-1	105	1.55	0.14	0.090	
2E-2	105	1.55	0.17	0.110	
2N	110	1.63	0.23	0.141	
2W	100	1.48	ND	--	6/6/95
2B	BLANK	--	ND	--	(1130-1330)
3S	180	2.21*	0.082	0.0371	
3E-1	180	2.66	0.17	0.0639	
3E-2	180	2.66	0.15	0.0564	
3N	180	2.66	0.11	0.0414	6/6/95
3W	185	2.74	ND	--	(1330-1630)
4S	195	2.89	0.050	0.0173	
4E-1	195	2.89	0.050	0.0173	
4E-2	195	2.89	ND	--	
4N	190	2.81	ND	--	6/6/95
4W	195	2.89	ND	--	(1630-1930)
5S	690	10.2	2.60	0.255	
5E-1	695	10.3	0.60	0.0583	
5E-2	695	9.90*	0.63	0.0636	
5N	690	9.35*	7.68	0.821	6/6-7/95
5W	690	10.2	3.25	0.319	(1930-0700)
6S	1440	21.3	18.04	0.847	
6E-1	1435	21.2	1.891	0.0892	
6E-2	1435	21.2	1.933	0.0912	
6N	1440	19.8*	19.69	0.994	6/7-8/95
6W	1440	21.3	19.98	0.938	(0700-0700)
7S	1450	21.5	1.94	0.0902	
7E-1	1445	20.6*	0.32	0.0155	
7E-2	1445	21.4	0.33	0.0154	
7N	1455	21.5	4.87	0.227	6/8-9/95
7W	1455	21.5	2.33	0.108	(0700-0700)

[1]All flows at 14.8 liters per minute unless otherwise noted.
*Flow had decreased at end of run, volume corrected. See SAMPLING METHODOLOGY.
ND = Not Detected, <0.030 ug/sample.
No values corrected for percentage of recovery.

TABLE III. Naled Meteorological Data

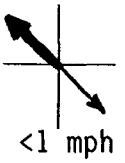
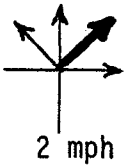
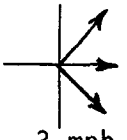
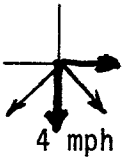
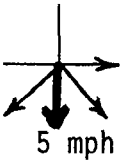
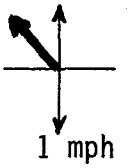
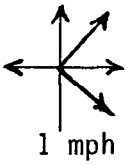
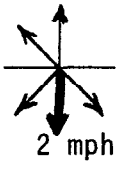
Sampling Period	Wind* Direction	Wind Speed (mph)	Cloud Cover
0	**SE**/NW	<1	PC
1	**SW**/S/W/SE	2	PC
2	W/NW/SW	3	PC
3	**N**/NW/W/NE	4	PC
4	**N**/NW/W/NE	5	PC
5	**SE**/S/N	1	PC
6	SW/W/NW/S/E	1	PC
7	**N**/NW/NE/SE/S	2	K

BOLD indicates predominant wind direction, if any.

*Indicates direction wind blows from.

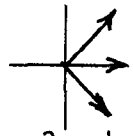
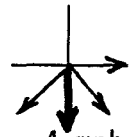
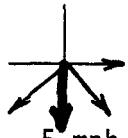
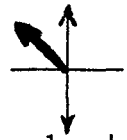
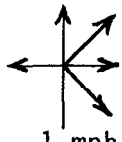
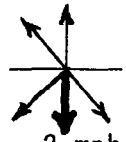
K = clear, PC = partly cloudy, O = overcast

TABLE IV. Summary of Naled Application Data (ug/m^3)

[N] ND (0) [W] ND  [E] ND <1 mph [S] ND	[N] 6.30 (1) [W] 1.23  [E] 3.02 2 mph [S] 0.0459
[N] 0.847 (2) [W] 0.0905  [E] 0.394 3 mph [S] 0.0684	[N] 0.135 (3) [W] 0.0157  [E] 0.176 4 mph [S] 0.145
[N] 0.0356 (4) [W] ND  [E] 0.0390 5 mph [S] 0.0519	[N] 2.16 (5) [W] 0.865  [E] 0.114 1 mph [S] 0.450
[N] 2.08 (6) [W] 0.952  [E] 0.161 1 mph [S] 1.04	[N] 0.246 (7) [W] 0.145  [E] 0.0174 2 mph [S] 0.0986

( ) Indicates sampling period. [ ] Indicates sampling site represented. Arrow indicates direction wind is blowing toward. **Bold** indicates predominant wind direction, if any.
ND = not detected, less than the limit of quantitation, 0.030 ug/sample.
[E] values are the average of 2 collocated samplers.

TABLE V. Summary of Dichlorvos Data (ug/m^3)

[N] ND (0) [W] ND  [E] ND <1 mph [S] ND	[N] 0.508 (1) [W] 0.129  [E] 0.412 2 mph [S] ND
[N] 0.141 (2) [W] ND  [E] 0.100 3 mph [S] ND	[N] 0.0414 (3) [W] ND  [E] 0.0602 4 mph [S] 0.0371
[N] ND (4) [W] ND  [E] 0.00865 5 mph [S] 0.0173	[N] 0.821 (5) [W] 0.319  [E] 0.0610 1 mph [S] 0.255
[N] 0.994 (6) [W] 0.938  [E] 0.0902 1 mph [S] 0.847	[N] 0.227 (7) [W] 0.108  [E] 0.0154 2 mph [S] 0.0902

( ) Indicates sampling period. [ ] Indicates sampling site represented.
Arrow indicates direction wind is blowing toward. **Bold** indicates predominant wind direction, if any.
ND = not detected, less than the limit of quantitation, 0.030 ug/sample.
[E] values are the average of 2 collocated samplers.